

Early Mars Climate Models

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Abstract. It is often stated that Mars and Earth had similar environmental conditions early in their history and that life might therefore have originated on Mars as well as on Earth. However, the atmospheric conditions required to produce and sustain a warm, wet climate on early Mars remain uncertain. State-of-the-art greenhouse models predict global mean surface temperatures early in Mars' history that differ little from today's, unless special conditions are invoked. The greatest difficulty the models have is coping with a faint early Sun.

1. Introduction

In spite of the failure of the Viking landers to detect life of any kind, Mars remains a high-priority target for exobiological investigations. The reason for this is the possibility that Mars and Earth experienced similar climatic conditions early in their history and that because life started on Earth, it might also have started on Mars. Then as the planets evolved, life flourished on Earth but became extinct on Mars. Certainly, the evidence for possible Martian microbes found in ALH84001 has heightened interest in this scenario [McKay *et al.*, 1996]. If confirmed, it would rank as one of the most significant discoveries in the history of civilization.

However, in spite of a great deal of work on the subject, our understanding of early Mars' climate history remains fuzzy. While the evidence for flowing liquid water in Mars' ancient terrains is compelling, a widely accepted mechanism for producing warm, wet conditions through climate change has yet to emerge. The main difficulty is dealing with the faint young Sun and finding a way to generate and sustain an atmosphere capable of producing a significant greenhouse effect.

As will become evident, our thinking about how the early Mars atmosphere could have produced a significant greenhouse effect has alternated between views concluding it could have, and those concluding it could not have. It is the classic *modus operandi* of scientific thinking; theories are proposed, scrutinized, revised, or abandoned altogether.

The purpose of this paper is to review the history of this fascinating subject to provide a context for where we presently stand on this issue. The paper draws heavily from related reviews by Carr [1996], Squyres and Kasting [1994], and Fanale *et al.* [1992] but emphasizes the climate models themselves and the processes they represent. The presentation is chronological, so that the reader can follow how our thinking has evolved with time.

2. Background

At the turn of the century the possibility that Mars had liquid water flowing on its surface was popularized in the writings of Percival Lowell, who envisioned vast canal systems constructed by intelligent beings struggling to survive on a dying planet. This romantic view of the red planet was convincingly dispelled

in the 1960s by the early Mariner spacecraft, which found no evidence for canals and, more important, near-surface temperatures and pressures that were simply too low for liquid water to be in equilibrium with the atmosphere [Ingersoll, 1970]. Moreover, Mars appeared to be a dead planet, having had a history much like that of Earth's Moon.

With Mariner 9, perspectives changed. Evidence for widespread fluvial activity, particularly in the older terrains, was found in images returned from the first Mars orbiter. Later, the Viking orbiters would reveal similar features. Liquid water was (and still is) thought to be the erosive agent that sculpted these features and while some could form under present climatic conditions (outflow channels), others could not (valley networks). Furthermore, the valley networks were found almost exclusively in the highly cratered ancient southern highlands, which date back to the end of the heavy bombardment period some 3.5–3.8 Gyr ago. While the precise mechanism by which the valley networks formed remains debatable (e.g., runoff versus sapping), the logical conclusion was that Mars must have had a warmer and possibly wetter climate very early in its history than it does today.

The easiest way to achieve warmer conditions early in Mars' history is through the greenhouse effect. In its simplest form, the greenhouse effect operates when solar radiation penetrates the atmosphere and is absorbed directly at the surface, which then radiates in the infrared. Greenhouse gases in the atmosphere absorb some of this upwelling radiation and reradiate it back to the surface. The net effect is to increase the surface temperature above the planet's effective temperature. The magnitude of the increase depends on which greenhouse gases are present and what their relative abundances are. It also depends on the abundance of nonabsorbing gases, since these can pressure broaden the lines if present in significant amounts. Candidate greenhouse gases and their principal absorption bands are shown in Figure 1.

A very potent greenhouse gas is ammonia (NH₃). Its vibrational fundamental at 10 μ m is in the middle of the so-called 8–12 μ m "window" region, and its weaker line at 16 μ m is near the peak of the Planck function for a 273 K blackbody. CO₂ also has a strong vibrational band at 15 μ m, several weak hot bands near 9 and 10 μ m, and pressure-induced transitions longward of 20 μ m. The latter become significant when pressures exceed several hundred millibars. But for CO₂ it is the 15 μ m band that provides the strongest interaction with infrared radiation. Water vapor has permitted rotational transitions longward of 20 μ m and a weak continuum absorption in the

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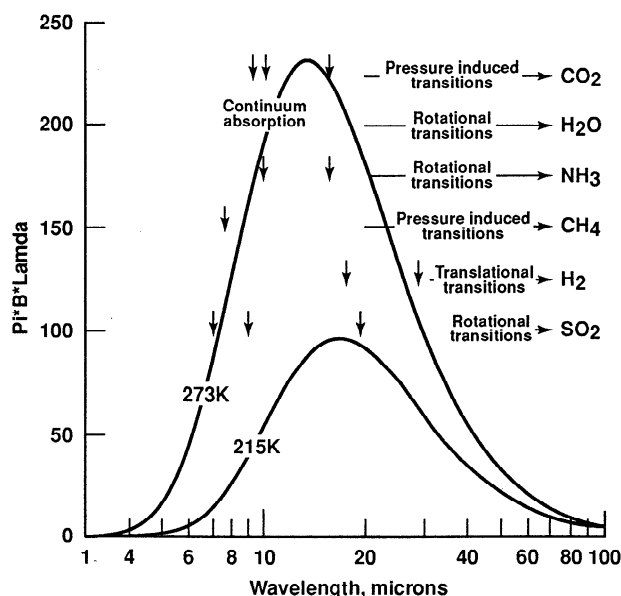


Figure 1. Planck function for temperatures of 215 and 273 K. Candidate Mars greenhouse gases and their principal absorption features are included.

window region that only plays a role when temperatures are well above 273 K. Methane's (CH_4) only permitted transition in the infrared at $7.7 \mu\text{m}$ puts it out on the short-wavelength tail of the Planck function, but at high enough partial pressures, its pressure-induced transitions longward of $20 \mu\text{m}$ can provide considerable opacity. The same is true for H_2 . Finally, SO_2 is a potentially powerful and potentially abundant greenhouse gas, having vibrational transitions near 7 , 9 , and $19 \mu\text{m}$ and rotational transitions longward of $40 \mu\text{m}$.

Were these greenhouse gases present in the early Martian atmosphere? For several reasons during the 1950s to 1970s it was generally believed that Earth's atmosphere, and Mars' by extension, was reducing early in its history. First, it was thought that planets accreted cold [Urey, 1952]. At low temperatures in H_2 -rich media the stable molecules are CH_4 , NH_3 , H_2S , and H_2O . Second, prebiotic organic compounds are readily synthesized in a reducing atmosphere, which is not the case for an oxidizing atmosphere [e.g., Miller and Urey, 1959]. Thus it was felt that an early reducing atmosphere must have existed; otherwise, life could not have begun. Third, a reducing atmosphere containing at least 10^{-5} ppm by volume of NH_3 could easily keep Earth from freezing-over early in its history, when the Sun was less luminous than it is today [Sagan and Mullen, 1972].

While reducing gases may have played some role, geochemists now believe that the early atmospheres of Mars and Earth were only weakly reducing and that CO_2 and H_2O were the dominant gases. There are two reasons for this. First, Earth's core now appears to have formed shortly after accretion at about 4.5 Ga [Stevenson et al., 1983]. Core formation on Mars also appears to have occurred at this time [Shih et al., 1982; Chen and Wasserburg, 1986]. The removal of metallic iron from the mantle should have left it in a relatively oxidized state, so that any gases vented from it should also have been oxidized. Second, reduced gases are photochemically unstable. Kuhn and Atreya [1979] showed that the NH_3 in Sagan and Mullen's primitive atmosphere would be consumed by ultraviolet pho-

tolysis in less than 10 years. Thus the NH_3 greenhouse, if it ever existed, was restricted to a period of extensive outgassing.

However, for Earth at least, there remains the problem of abiotic synthesis of amino acids and other organic compounds in an oxidizing environment. This would also be an issue for Mars if the claim by McKay et al. [1996] for an early Martian biota is confirmed. The problem is most easily mitigated if, indeed, reducing gases were present in the early atmosphere. Fanale [1971] proposed a mechanism by which Mars could have catastrophically developed a substantial reducing atmosphere during accretion that may have lasted for as long as 10^8 years. However, we are more interested in the period between 4.0 and 3.5 Ga, which is long after hydrodynamic escape would have removed any primary atmosphere [e.g., Pepin, 1994]. Instead, reducing conditions during this period might have been generated by recycling volatiles through the mantle, as has been proposed for Earth [Kasting et al., 1993]. Alternatively, reduced material and volatiles could have been delivered by comets [Chyba, 1990; Owen and Bar-Nun, 1995]. In the end, however, we simply do not know if reducing conditions existed on Mars and if so for how long. The present consensus is that CO_2 and H_2O were the dominant gases during the period of interest.

CO_2 by itself is not a particularly effective greenhouse gas, since it absorbs mainly in the $15 \mu\text{m}$ band. Water, of course, has many features in the infrared but is now a minor constituent. However, in combination, the two gases work well if the water vapor abundance is tied to the temperature field. This is a reasonable assumption if there are ample supplies at the surface (e.g., oceans). In this way, water vapor can significantly amplify the greenhouse effect of CO_2 alone. Thus the issue becomes how much CO_2 is required to produce a significant greenhouse effect and is that amount consistent with 5–10 bars estimated for the total inventory? (See Fanale et al. [1992] for a review of the Martian volatile inventory.)

It is worth noting at this point what opacity is required to generate enough greenhouse warming on early Mars to reach the melting point of water. According to stellar evolution models [e.g., Newman and Rood, 1977; Gough, 1981], the Sun's luminosity at 3.8 Ga was 75% of its present value. Assuming the planet's albedo was the same as it is today (~ 0.25), its effective radiating temperature T_e would have been $\sim 196 \text{ K}$. If a global mean surface temperature T_s of 273 K or higher is required to sustain liquid water at the surface, then the atmosphere must provide at least 77 K of greenhouse warming. To achieve this, the grey infrared transparency of the atmosphere, $(2(T_s/T_e)^4 - 1)^{-1}$, can be no more than about 15%. In other words, the early Martian atmosphere must intercept at least 85% of the radiation coming up from the surface. This is much greater than the 56% absorbed by Earth's present atmosphere but considerably less than the 99% absorbed by Venus' present atmosphere. Clearly, this is a major challenge for early Mars greenhouse models.

3. Greenhouse Models

During the 1970s and 1980s, three classes of greenhouse models were constructed: global average energy balance models [Sagan and Mullen, 1972; Sagan 1977]; one-dimensional (1-D) radiative-convective models [Pollack, 1979; Cess et al., 1980; Pollack et al., 1987], and latitudinally resolved energy balance models [Hoffert et al., 1981; Postawko and Kuhn, 1986].

Table 1. Mass and Composition of Early Mars Atmosphere Required to Raise Global Annually Averaged Surface Temperatures to 273 K

Model	Comment
<i>Sagan</i> [1977]	1 bar H ₂
	1 bar foreign gas + minor amounts of NH ₃
<i>Pollack</i> [1979]	10 bar CO ₂ -H ₂ O
	0.6 bar CO ₂ + minor amounts of NH ₃ , CH ₄ , H ₂
<i>Cess et al.</i> [1980]	Did not consider early Mars
<i>Hoffert et al.</i> [1981]	Did not consider early Mars
<i>Postawko and Kuhn</i> [1986]*	~10 bar CO ₂ -H ₂ O + minor amounts SO ₂
<i>Pollack et al.</i> [1987]	5 bars CO ₂ -H ₂ O
<i>Kasting</i> [1991]	No amount of a CO ₂ -H ₂ O atmosphere is capable of warming the surface to 273 K
<i>Forget and Pierrehumbert</i> [1997]	0.5–2 bars, depending on amount of water available and on the opacity of CO ₂ ice clouds
<i>Yung et al.</i> [1997]	2 bars CO ₂ plus 0.1 ppmv SO ₂

*Postawko and Kuhn performed calculations for atmospheres containing up to 3 bars of CO₂ and were not able to warm the surface to 273 K. The 10 bar figure given here is based on an extrapolation of the rightmost curve in Figure 3.

We first briefly describe these models and then chronologically discuss their contributions.

The global energy balance model of *Sagan and Mullen* [1972] and *Sagan* [1977] is the simplest of the models we will discuss. The model balances the globally averaged absorption of sunlight with infrared emission. The outgoing infrared is calculated in terms of a contribution from the surface and one from the atmosphere. The latter was calculated by assuming a single isothermal layer with temperature $2^{-1/4}T_e$ using wavelength-integrated emissivities for the bands of interest. This is the simplest possible representation of the vertical thermal structure of the atmosphere.

The 1-D radiative-convective models, on the other hand, divide the atmosphere into a number of vertical layers but still ignore latitudinal variations. The temperature structure is found by first balancing the solar and infrared fluxes within each layer so that no net heating occurs, and then performing an adjustment to the temperature profile in those regions where the lapse rate exceeds some specified value. The calculated radiative fluxes depend on the abundance and distribution of absorbers, which bands are considered, the method used to solve the radiative transfer equation, and the accuracy of the opacity coefficients. In general, the optically active gases are assumed to be uniformly mixed except for water vapor, which is indexed to a relative humidity profile. The lapse-rate adjustment in the 1-D models is meant to simulate the stabilizing effect of a variety of atmospheric phenomena (dry/moist convection, large-scale motions) that cannot be explicitly calculated in these models.

It is important to note the role of the lapse-rate adjustment on the calculated surface temperature in 1-D models. If the lapse rate is high (static stability low), surface temperatures will be warmer than if the lapse rate is low (static stability high). This is because a high lapse rate yields a cooler upper atmosphere, which then radiates less to space. To maintain energy balance, the surface temperature must increase. In the models discussed below, the lapse rate has been assumed to vary between dry and moist adiabatic values. The difference depends on the water vapor content and can be about a factor of 2 at 300 K, so this is an important effect.

In latitudinally resolved energy balance models the net radiative loss (gain) at the top of the atmosphere at a given latitude is balanced by heating (cooling) due to atmospheric

transport from neighboring latitudes. These models treat the outgoing infrared as a linear function of surface temperature, which is empirically derived from Earth data. Atmospheric transport is represented as a diffusive process. In both cases the representations are crude. This is done in order to allow for latitudinal variations and yet retain some simplicity. These models have roots in the terrestrial climate studies of the late 1960s, which showed Earth's climate system to be very sensitive to changes in solar insolation [*Budyko*, 1969; *Sellers*, 1969].

In discussing the results of these models, we will focus on global and annual averaged surface temperatures. This not only facilitates comparison, but it is the appropriate measure for determining the stability of liquid water. While it is true that surface temperatures can reach the melting point at certain times and in certain locations while the global annual mean temperature is below freezing, these conditions are marginal and difficult to interpret. We shall return to this point below, but for now, we assume that a global and annually averaged surface temperature at or above 273 K is required to stabilize liquid water on the surface of early Mars. Thus in Table 1 we present the mass and composition of the primitive Martian atmosphere that meets this requirement for each of the models discussed below.

Sagan [1977] calculated several possible evolutionary tracks for a Mars atmosphere whose initial mass and composition was (1) 1 bar hydrogen, (2) 1 bar of a foreign gas with NH₃ as a minor constituent in equilibrium with clay minerals, and (3) a low-pressure CO₂-H₂O atmosphere comparable to the present-day atmosphere. In atmosphere 2 the foreign gas serves to pressure broaden the NH₃ lines. The results are shown in Figure 2 and clearly indicate the powerful greenhouse effect of reducing atmospheres. Both the hydrogen-rich and the equilibrium NH₃ atmospheres give temperatures near 273 K at 3.8 Ga. However, if the hydrogen was outgassed at the end of accretion during core formation, as seems likely, it would have escaped to space by hydrodynamic blowoff long before 3.8 Ga, and NH₃ has the stability problem mentioned earlier. So these atmospheres seem unlikely.

Pollack [1979] carried out two sets of calculations for Mars with his 1-D model: one for a CO₂-H₂O atmosphere, and one for a CO₂-H₂O atmosphere containing reducing gases (NH₃, CH₄, H₂) with specified mixing ratios. The mixed oxidation state of this latter atmosphere was thought to represent the

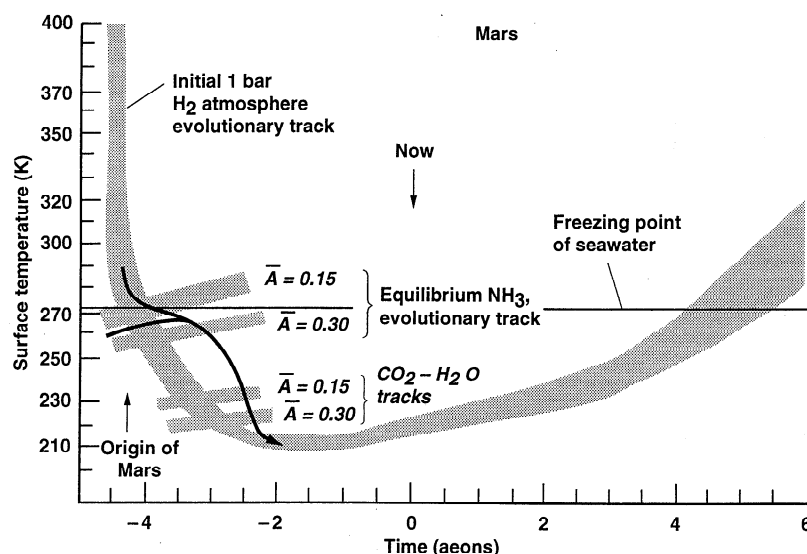


Figure 2. Evolutionary tracks for Mars' surface temperature for three initial atmospheric compositions and two different albedos [from *Sagan, 1977*].

transition from a putative early reducing atmosphere to a fully oxidized atmosphere. For the purely oxidizing atmosphere, nearly 10 bars of CO_2 were required to raise global mean temperatures to the melting point of water early in Mars' history (2 bars is often quoted for this case in the literature, but this figure applies only to present-day conditions); for the reducing atmosphere only 0.6 bar was required. Clearly, the purely oxidizing atmosphere is pushing the upper limit on the estimated maximum amount available.

Cess et al. [1980] presented results from their 1-D model, which included a more detailed treatment of several CO_2 hot bands (10, 12, 18 μm), the water vapor continuum, and the change in planetary albedo due to Rayleigh scattering. Unfortunately, their claim that much less CO_2 could warm the surface to the melting point than found by *Pollack* [1979] must be disregarded due to a coding error.

The first latitudinally resolved energy balance calculations were published by *Hoffert et al.* [1981]. They noted the lack of sufficient data for Mars to form a correlation between surface temperature and outgoing infrared flux, and so developed band absorptance models for CO_2 and H_2O . Their results, which apply to present solar luminosity, were similar to that of *Cess et al.* [1980] in that <1 bar CO_2 was sufficient to raise global mean surface temperatures to 273 K. However, in the 0.1–0.5 bar range, their surface temperatures were well above (by up to 25 K) those found by *Pollack* and *Cess et al.* It is not certain why there is such a large discrepancy, but it must be at least partly related to their assumption that the lapse rate varies exponentially with height, and that the "stratospheric" temperature is fixed at 160 K. Since much of the outgoing radiation in the 15 μm band originates at high levels, lower temperatures at these levels will require higher surface temperatures to maintain energy balance.

The work of *Pollack* [1979], *Cess et al.* [1980], and *Hoffert et al.* [1981] emphasized climate change for present solar luminosity. It is not clear why these authors gave so much attention to present conditions when it was well known that the valley networks were formed when the solar output was greatly reduced. This was unfortunate, since it conveyed a sense that 1–3 bars (or less) of CO_2 was all that was needed to produce a

strong enough greenhouse effect to stabilize liquid water early in Mars' history. It wasn't until the end of the 1980s that the emphasis clearly shifted to early Mars.

The first study to strictly focus on early Mars was by *Postawko and Kuhn* [1986], who used a latitudinally resolved energy balance model similar to that of *Hoffert et al.* [1981], but with different assumptions regarding the tropospheric lapse rate and stratospheric temperature. The tropospheric lapse rate was fixed at the dry adiabatic value (~ 5 K/km), and stratospheric temperatures were allowed to vary with latitude. (Note that this lapse-rate assumption will give maximum surface temperatures.) They examined the surface heating resulting from atmospheres containing CO_2 alone, and those with additional amounts of SO_2 and H_2O . The result (Figure 3) shows how difficult it is to raise surface temperatures to the melting point in the presence of a faint young sun. Under optimal conditions (3 bars of CO_2 plus SO_2 and H_2O), a greenhouse warming of ~ 55 K can be realized. However, this is still short of the ~ 77 K that is required to reach the melting point of water.

Postawko and Kuhn [1986] also illustrated the potential role of atmospheric heat transport in controlling surface temperatures. As shown in Figure 4, heat transport controls the equator-to-pole temperature gradient: the greater the transport, the weaker the gradient. This is important for two reasons. First, it means that 1-D radiative-convective models will overestimate surface temperatures in equatorial regions, since they do not account for heat loss by transport. The difference can be as much as 25 K, depending on the vigor of transport. Second, if heat transport is too weak, then polar temperatures may fall below the CO_2 frost point temperature. In this situation, permanent polar caps would form and surface pressures would fall until reaching equilibrium. For a 3 bar CO_2 atmosphere the frost point temperature is 208 K. Thus Figure 4 suggests that Mars may not have been able to sustain a 3 bar atmosphere early in its history.

The second paper published in the late 1980s that focused on early Mars was by *Pollack et al.* [1987]. They refined *Pollack's* [1979] 1-D greenhouse model by including improved values of CO_2 and H_2O opacities, and by allowing for the CO_2 pressure-induced transitions, the 8–12 μm water vapor con-

tinuum, a variety of weak lines for both gases, and the change in planetary albedo due to Rayleigh scattering. They also assumed a moist adiabatic lapse in the troposphere and a relative humidity that decreased with height somewhat analogous to present conditions on Earth. Figure 5 summarizes their results. With this improved model, the amount of CO_2 required for surface melting is reduced from Pollack's earlier calculations by about a factor of 2. For the 0.7 times present solar luminosity case, global mean surface temperatures reach 273 K for a surface pressure of about 5 bars.

4. Maintaining a Dense CO_2 Atmosphere

By the end of the 1980s the paradigm for early Mars was based on the Pollack *et al.* [1987] model. The amount of CO_2 required to raise the global mean surface temperature to 273 K was thought to be ~ 5 bars. Though large, this amount was still consistent with estimates of the available inventory. The question then became how to maintain it long enough to form the fluvial features and erode the surface. Two processes should act to deplete atmospheric CO_2 on geologically short time-scales: impact erosion and weathering.

Large impacts can remove part or all of the overlying atmosphere by creating an outwardly expanding plume. The amount of mass ejected depends on the size the impactor, its composition, and its impact velocity. Melosh and Vickery [1989] developed a simple analytic model of impact erosion to estimate these attributes. They calculated a minimum impact velocity of 11–14 km/s depending on the ice content of the impactor. Velocities less than this would not create a plume capable of exceeding the escape velocity. They determined the size of the impactor by requiring its plume mass to exceed the mass of the atmosphere above the plane tangent to the impact point. For

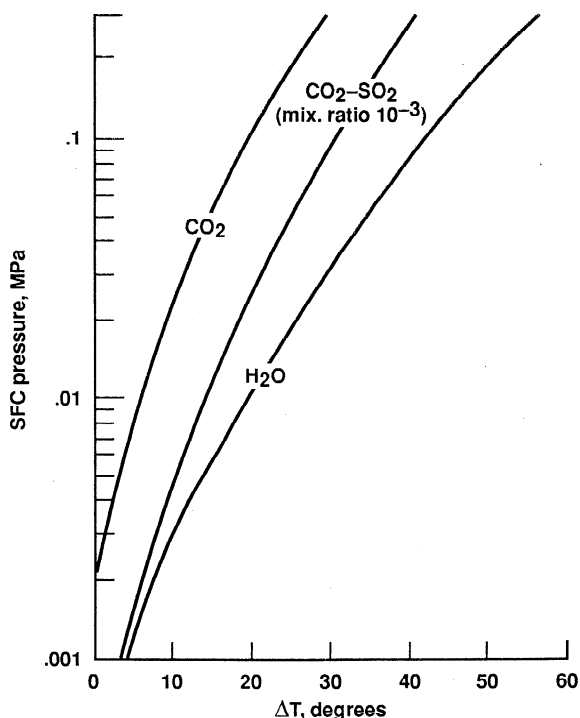


Figure 3. Greenhouse surface heating for a pure CO_2 atmosphere, and atmospheres containing SO_2 and H_2O [from Postawko and Kuhn, 1986].

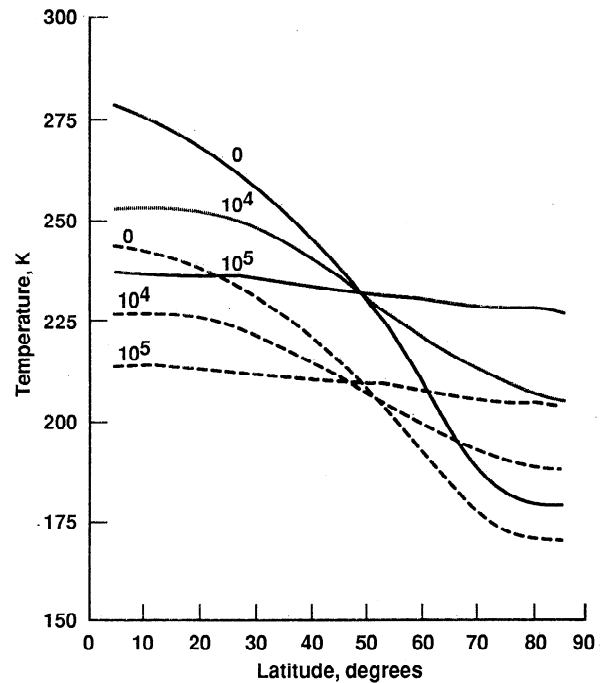


Figure 4. Surface temperatures for a 3 bar pure CO_2 atmosphere. Heavy lines are for present solar luminosity. Light lines are for 75% of present solar luminosity. Lines are labeled with the value of the eddy diffusion coefficient (mks) [from Postawko and Kuhn, 1986].

present Mars conditions, a silicate object 3 km in diameter satisfies this requirement. Using the lunar record to estimate the cratering rate, Melosh and Vickery's model predicted the evolutionary history of the atmosphere shown in Figure 6.

According to their model, the Martian atmosphere was about 100 times its present mass after accretion but then was rapidly eroded to near its present mass by the end of the heavy bombardment. There are several concerns with this scenario. First, this initial amount of CO_2 is much less than needed for significant global greenhouse warming. Second, much of the

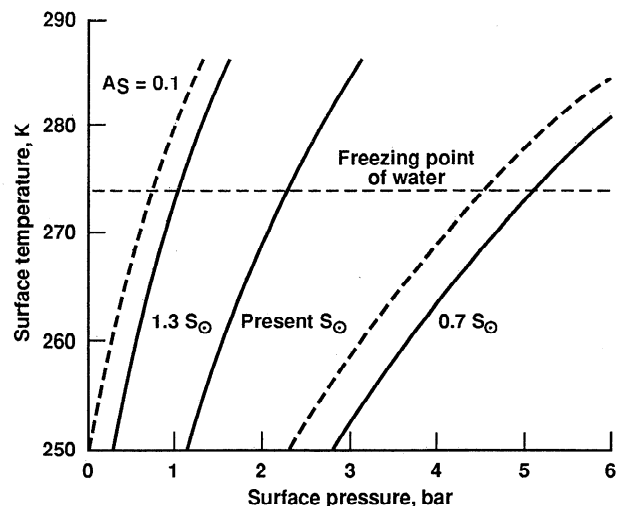


Figure 5. Surface temperature as function of surface pressure for several values of the solar luminosity. Dashed lines assume a surface albedo of 0.1 [from Pollack *et al.*, 1987].

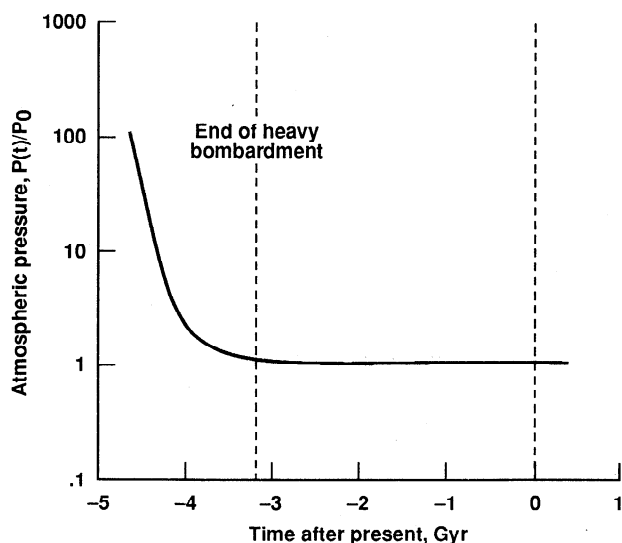


Figure 6. Evolution of atmospheric pressure $P(t)$ relative to its present value P_0 [from Melosh and Vickery, 1989].

atmosphere is removed prior to the end of the heavy bombardment, in which case even less greenhouse warming would be generated during the period when it is most needed. Finally, the model severely restricts the size of the initial atmosphere. Nevertheless, the observed relative excess of ^{129}Xe and ^{40}Ar is consistent with an early epoch of impact erosion [Owen, 1992; Zahnle, 1993]. By systematically reducing the mass of the initial atmosphere before these radiogenic isotopes are released, it is possible to increase their relative abundances. Furthermore, Mars is particularly vulnerable to impact erosion because of its small size. Consequently, this process is likely to have operated at some level early in Mars' history.

Weathering is a process that converts atmospheric CO_2 into carbonate rock. On Earth, CO_2 in the atmosphere dissolves in rainwater, creating a mild carbonic acid solution. As this acidified rainwater flows from land to sea, it interacts with silicate and carbonate rocks, producing cations (e.g., Ca^{2+} , Mg^{2+}) and anions (HCO_3^{2-}). These then accumulate in the oceans, where they are taken up by organisms that convert them back into carbonates for incorporation into shells and hard parts. When these organisms expire, they settle to the ocean floor. However, it is important to realize that carbonate formation would still occur in the absence of shell-forming biota. The cation and anion concentrations would simply increase until carbonates formed abiotically. Ultimately, the rate of carbonate formation would be independent of which process is occurring, since at steady state the loss of cations and anions must be equal to the gain from runoff.

Pollack *et al.* [1987] estimated weathering rates for Mars by multiplying the present weathering rate on Earth by a number of scaling factors. These included the dependence of the weathering rate on pressure, the dependence of runoff and the weathering reaction itself on temperature, the cation content of the rocks, and the fraction of the surface containing open bodies of liquid water. For some of these, Pollack *et al.* chose rather conservative values. For example, they assumed that only 5% of the planet's surface was covered with liquid water. Overall, they estimate a factor of 2 uncertainty in their weathering rates. The results are shown in Figure 7.

Clearly, Pollack *et al.*'s calculations indicate that the weath-

ering lifetime of any early Mars atmosphere is rather short. A 5 bar atmosphere at 273 K, for example, has a lifetime of ~ 50 Myr, about an order of magnitude less than the timescale of interest. Fanale *et al.* [1982] also predicted short weathering lifetimes for 1–2 bar CO_2 atmospheres. Thus some resupply of CO_2 is indicated if the greenhouse effect is to persist over an extended period.

However, more recent calculations by Schaefer [1993] suggest much longer weathering lifetimes than predicted by Pollack *et al.* Her calculations were based on an explicit model of a geochemical system (Figure 8). Thus her approach is fundamentally different from the scaling approach adopted by Pollack *et al.* The model consists of an unweathered starting material (Ca-Mg silicates), a CO_2 atmosphere, an ocean in simultaneous contact with the unweathered material and the atmosphere, and the chemistry of carbonate (calcite and dolomite) precipitation. Her baseline model starts with a 1 bar CO_2 atmosphere, a 273 K ocean covering 30% of the surface to a depth of 1 km, and a 1 km deep unweathered regolith. The key result, namely, that a 1 bar atmosphere is consumed in 500 Myr rather than 50 Myr, is shown in Figure 9. Since Schaefer did not allow the ocean temperature to fall as CO_2 (and the greenhouse effect) declined, an even longer timescale is implied.

Schaefer did not discuss the reason for the large difference in her calculated weathering lifetimes compared to those of Pollack *et al.* [1987]. One possibility is the low initial $p\text{H}$ of the ocean, which would tend to inhibit carbonate precipitation. The $p\text{H}$ of Earth's oceans is ~ 8 , which is considerably higher than shown in Figure 9. But other factors could be involved. An interesting result of Schaefer's longer weathering lifetimes is that they imply that the atmosphere could not have begun with more than several bars of CO_2 . Otherwise, the present atmosphere would be larger than it is. In this case, removal of CO_2 by some other means is required. This is exactly opposite the conclusion reached by Pollack *et al.*

Nevertheless, by the end of the 1980s, several ways to stabilize CO_2 against what was believed to be rapid conversion to carbonates were suggested. Pollack *et al.* [1987] estimated the resupply of CO_2 by volcanic burial of carbonate deposits. Heat flow, and by implication, volcanic activity, is thought to have been higher in early Mars' history [e.g., Schubert *et al.*, 1992]. Volcanic activity can supply CO_2 directly by venting or by thermally decomposing existing carbonate deposits. The latter can occur when hot lava comes in contact with the carbonates

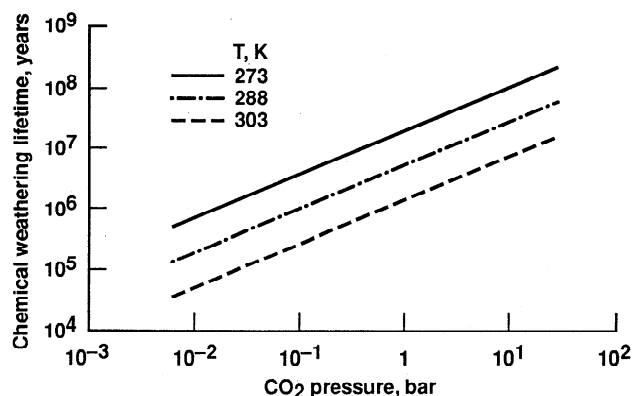


Figure 7. Chemical weathering rates as a function of surface pressure [adapted from Pollack *et al.*, 1987].

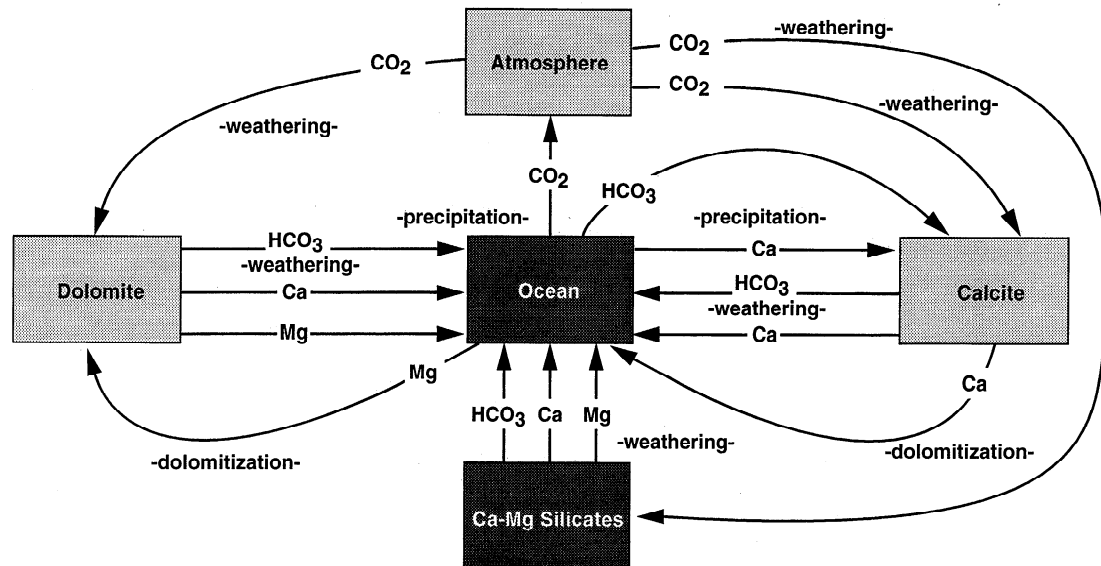


Figure 8. A schematic diagram of a hypothetical geochemical cycle for early Mars [from Schaefer, 1993].

or when it buries them to sufficient depth to reach the decomposition temperature. Pollack et al. estimated the timescale for direct venting and burial recycling by splitting the surface heat flux into a part delivered by conduction and a part delivered by cooling lava. The results are shown in Figure 10. Evidently, the juvenile contribution is too slow to resupply weathered CO_2 . Recycling by burial, however, can be very effective for the heat flows expected on early Mars ($\sim 150 \text{ mW m}^{-2}$). Thus, if weathering on early Mars was rapid, a means to recycle it has been identified.

Another way to recycle weathered CO_2 is by impacts. Impacts can recycle CO_2 several ways. First, the impact ejecta can accumulate to sufficient depth to initiate thermal decomposition of the carbonates it buries. Second, carbonates can be decomposed directly by the shock heating associated with the impact itself. Impactors can also deliver CO_2 directly to the planet, depending on their composition. Carr [1989] used simple models to get an order of magnitude estimate of the relative contribution of each of these processes. He found that, even in combination, impact recharge was not a very effective

process, as it was capable of providing only about several tenths of a bar of CO_2 in a 10 Myr period. Higher recharge rates are possible if all the impactors were carbonaceous chondrites, but this is unlikely. Carr concluded that previous estimates of the CO_2 weathering rates were too large. The subsequent work by Schaefer [1993] supports this view and further complicates the issue of disposing a massive early atmosphere.

5. Challenges

The warm and wet early Mars hypothesis was seriously challenged in 1991, when Kasting published his reanalysis of the Pollack et al. [1987] greenhouse calculations. Kasting noted that at the higher pressures, CO_2 can condense in the atmosphere and that this can have two important effects. First, latent heat released by the condensing CO_2 will increase atmospheric temperatures. If all else remains the same, this means that surface temperatures must cool in order to maintain the same outgoing flux at the top of the atmosphere. Thus atmospheric condensation of CO_2 will decrease the greenhouse effect. An example of this effect from Kasting's [1991] paper is shown in Figure 11. Second, the condensing CO_2 will form clouds which can alter the solar and infrared fluxes. Pure CO_2 clouds are likely to lower surface temperatures, since they should be good scatterers at solar wavelengths and poor absorbers at infrared wavelengths. However, Kasting simply noted that this would make things worse, and so he only considered the effect of CO_2 condensation on the temperature profile, not the radiative effects of the clouds themselves.

To do this, Kasting modified the lapse-rate adjustment scheme in the Pollack et al. model. In regions where CO_2 was condensing, the temperature profile was constrained to follow a moist CO_2 adiabat (i.e., the saturation vapor pressure curve). He then repeated the earlier calculations and found that while condensation throttling of the greenhouse effect was relatively modest for present solar luminosity, it was very effective for luminosities appropriate to early Mars. At 75% present solar luminosity, condensation reduces surface temperatures in a 1 bar atmosphere by about 15 K compared to what they would be without condensation. What is more important, CO_2 condensation limits the amount of CO_2 an atmosphere can support,

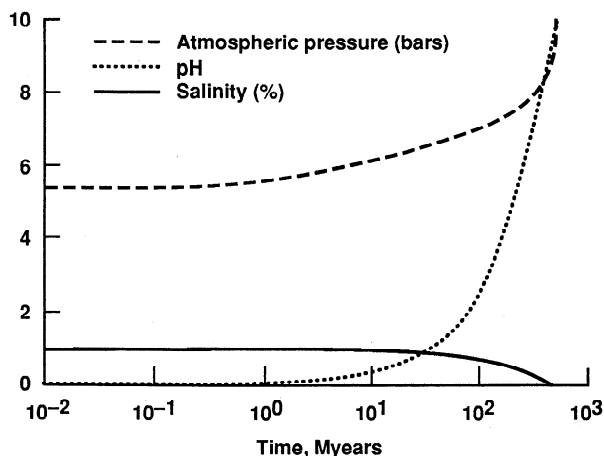


Figure 9. Variation of surface pressure, pH, and ocean salinity with time as simulated by the geochemical model of Figure 6 [from Schaefer, 1993].

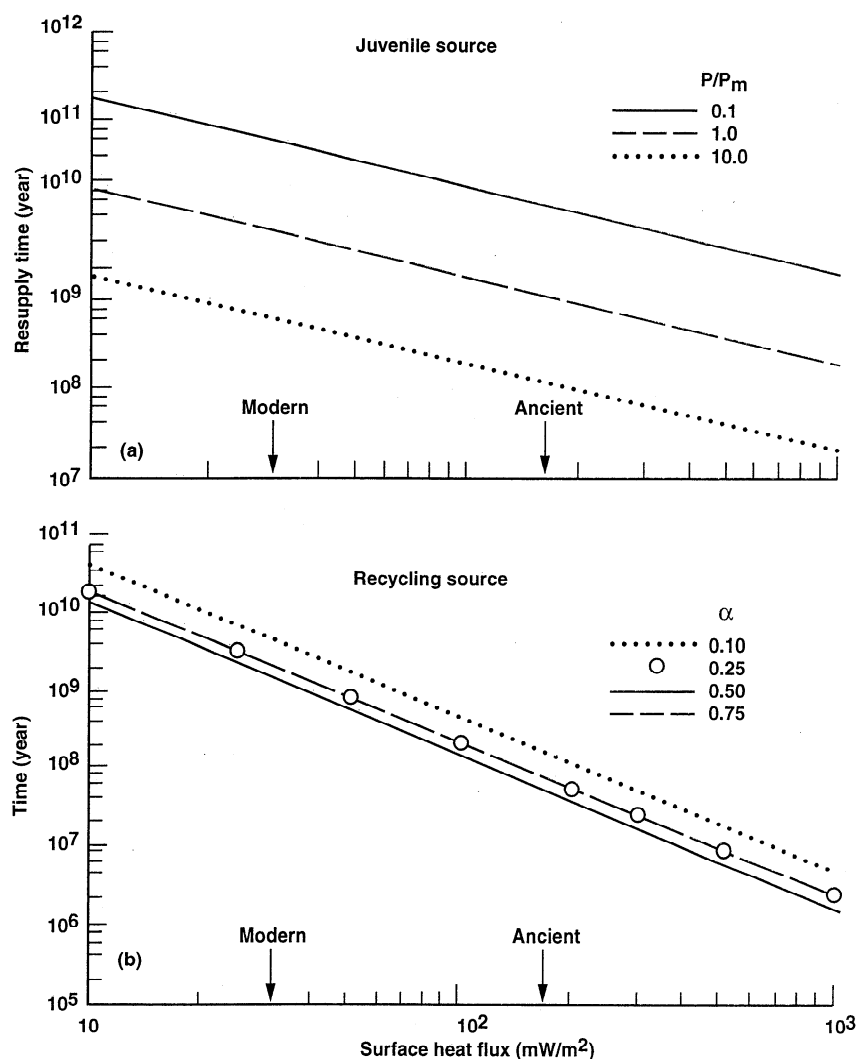


Figure 10. Timescale for resupplying CO₂ as a function of the surface heat flux. (a) Outgassing of juvenile CO₂ for three different values of the ratio of atmospheric to mantle CO₂ (P/P_m). (b) recycling by volcanic burial for different values of the fraction of heat carried by thermal conduction (α) [from Pollack et al., 1987].

since ultimately, the entire atmosphere saturates. According to Figure 12, this saturation limit is about 2.5 bars at 75% present luminosity. Surface temperatures at this pressure are only about 220 K. This implies that early Mars surface temperatures would have differed little from present-day values.

Another challenge for the warm and wet hypothesis is the disposal of a massive early CO₂ atmosphere. Even if CO₂ condensation could be avoided (say, by the addition of trace greenhouse gases or dust particles; see below), 1–5 bars of CO₂ would still be needed to raise mean temperatures to the melting point. What has been the fate of this early atmosphere? The candidate reservoirs are illustrated in Figure 13.

Incorporation into the carbonate rock reservoir is an obvious choice, but once temperatures fall below freezing and liquid water is no longer stable, weathering rates are greatly reduced. A minimum of 1 bar of CO₂ would need to be weathered at subfreezing temperatures. Dry carbonate formation has been suggested [Booth and Kieffer, 1978; Stephens and Stevenson, 1990], but the kinetics of this reaction have yet to be quantified. Carbonate formation might also occur in transitory

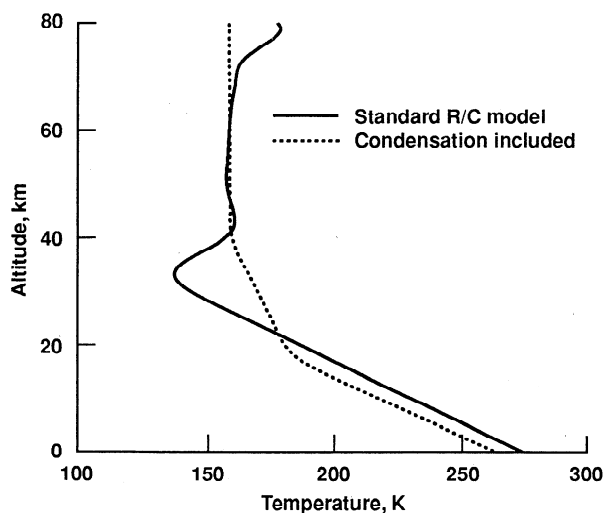


Figure 11. Temperature profiles for a 2 bar CO₂ atmosphere with and without CO₂ condensation, and for present solar luminosity [from Kasting, 1991].

pockets of liquid water that are in disequilibrium with the environment [Kahn, 1985]. Such pockets of water are capable of forming with overlying pressures as low as 20 mbar. While it is not clear that the necessary conditions for this process, i.e., water, heat, and cations, occur at the same place and same time, the fact that the present surface pressure is close to the triple point of water does provide support for this idea.

Other reservoirs for an early Mars atmosphere are the regolith, the polar caps, and space. A global 1 km deep nontro-nite clay regolith could hold as much as 1 bar of CO₂ [Fanale *et al.*, 1982], but such a regolith is unlikely. An upper limit of several hundred millibars seems more reasonable. The amount of CO₂ stored in the polar caps is also difficult to estimate. The permanent cap in the south probably contains no more than several millibars of CO₂ at the present time. Some CO₂ could be buried in the polar regions [Jakosky *et al.*, 1995], but basal melting will limit the total to something of the order of several tens of millibars [Mellon, 1996].

CO₂ can also escape to space. The carbon in CO₂ can escape nonthermally [McElroy, 1972], or the entire molecule can be ejected by sputtering of reentering O⁺ pickup ions [Luhmann *et al.*, 1992]. Sputtering is by far the most significant escape mechanism, and Luhmann *et al.* estimate a time-integrated loss of ~0.15 bar. However, there is considerable uncertainty in this estimate, since the escape rates are very sensitive to the solar EUV flux and the dissociation efficiency of each collision [Kass and Yung, 1995; Johnson *et al.*, 1996].

If we adopt upper limits for the size of each of these reservoirs, then they can account for about 1 bar of CO₂. That means the carbonate reservoir must contain 0–4 bars of CO₂ if the warm and wet early Mars hypothesis is correct. While there is some evidence for carbonates in atmospheric dust particles [Pollack *et al.*, 1990], and while carbonates have been found in the SNC meteorites [Gooding *et al.*, 1988], they have been difficult to detect thus far. Preliminary estimates from the Mars Global Surveyor orbiter put an upper limit on exposed carbonate deposits of <10% for the limited regions observed thus far [Christensen *et al.*, 1998].

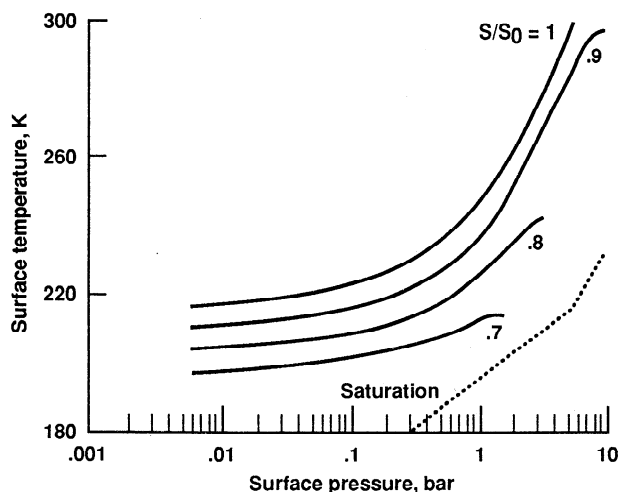


Figure 12. Surface temperature as a function of surface pressure for four different values of the solar luminosity. Dashed line shows the saturation vapor pressure of CO₂. For the 0.7 and 0.8 luminosity cases, pressures greater than the maximum permitted would discontinuously move the curves down to the saturation vapor pressure [from Kasting, 1991].

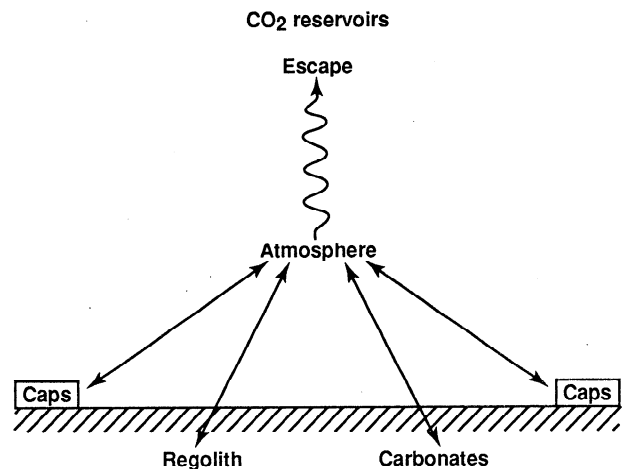


Figure 13. Candidate reservoirs for an early CO₂ atmosphere.

A further difficulty with the warm, wet hypothesis is that it is very difficult to arrive at present-day conditions starting from a massive early atmosphere. This was illustrated by Haberle *et al.* [1994], who constructed a model for the evolution of CO₂ on Mars based on published estimates of the processes believed to be relevant to the fate of CO₂. The model calculated equatorial and polar temperatures as a function of time, allowing for the change in solar luminosity, the greenhouse effect, the removal of CO₂ by weathering, storage in the regolith, and polar cap formation. According to their calculations, shown in Figure 14, 80% of a 5 bar atmosphere would be weathered into carbonates. The remaining 20% would be evenly split between the regolith and permanent caps. As noted above, 0.5 bar stored in the regolith and another 0.5 bar stored in the caps is unrealistic.

6. Possible Solutions

It is clear that pure CO₂/H₂O atmospheres have great difficulty producing enough greenhouse warming to sustain warm and wet conditions early in Mars' history. Yet the evidence for such conditions is compelling. There are several possible solutions. Beginning with the most promising, and progressing to the least likely, these are listed as follows.

6.1. CO₂ Ice Clouds Create a Scattering Greenhouse Effect

If the ice crystals in CO₂ clouds grow big enough, they may scatter thermal radiation back to the surface, thereby reducing the outgoing infrared flux and increasing surface temperatures. For this to occur, the particles must grow to >5 μm, and they must remain in the atmosphere long enough to have an effect. There is a good chance these conditions can be fulfilled. Unlike water ice crystals in Earth's atmosphere whose growth is limited by diffusion of water vapor through air, CO₂ ice crystals should grow by direct hydrodynamic flow, since CO₂ is the main constituent of the atmosphere. Thus CO₂ ice crystals might easily grow to sizes capable of scattering thermal radiation.

Recently, Forget and Pierrehumbert [1997] have shown that a CO₂ ice cloud scattering greenhouse can be quite powerful. They demonstrated this by modifying the upward and downward infrared fluxes in each spectral interval of Kasting's [1991] model by assuming a single-layer cloud. The transmissivity,

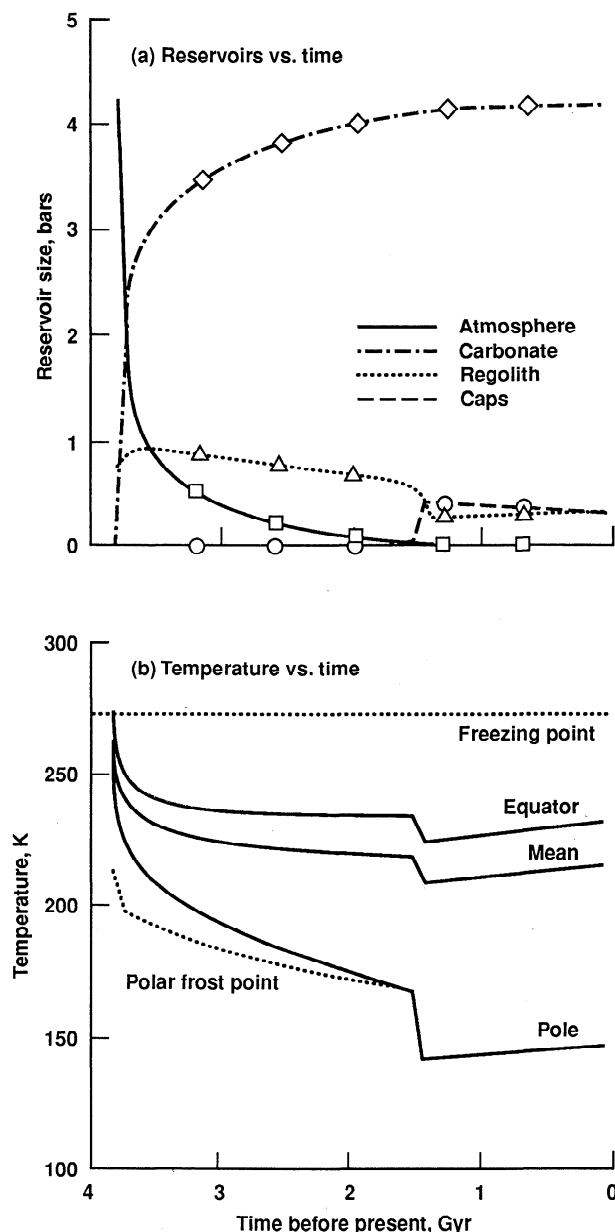


Figure 14. (a) Evolution of various CO₂ reservoirs as a function of time. (b) Surface temperatures as a function of time [adapted from Haberle *et al.*, 1994].

emissivity, and reflectivity of the cloud were determined from a two-stream code using single scattering properties obtained from Mie theory with Hansen's [1997] refractive indices and a modified gamma size distribution. For CO₂ ice clouds with optical depth 10 and mean particle sizes in the 10–50 μm range, global mean surface temperatures of 273 K can be reached for surface pressures ranging from 0.5 to 2 bars depending on how much water vapor is available. Compared to the ~ 220 K mean surface temperatures that result for this pressure range when cloud radiative effects are ignored, this result clearly indicates the potential importance of a scattering greenhouse effect for early Mars.

The scattering greenhouse is perhaps the most promising solution to the early Mars climate dilemma. However, much work remains before it can be confirmed. Continued microphysical studies of the nucleation, growth, and sedimentation

of CO₂ ice crystals of the kind initiated by Wood *et al.* [1996] are needed. Ultimately, a 3-D calculation with coupled transport, microphysics, and radiative effects will be needed to better assess what fraction of the planet CO₂ clouds would occupy and what opacities they might have. It is worth noting that unlike water clouds on Earth, which have a cooling effect [Ramanathan *et al.*, 1989], CO₂ ice clouds on Mars would have a warming effect. This is a negative feedback which would limit the cloud ice content.

6.2. Greenhouse Gases Other than CO₂/H₂O Play a Role

While oxidized atmospheres are generally favored for early Mars, it is still possible that reduced gases, such as CH₄ and NH₃, have played a role. Kasting [1991] argued that this is the most promising solution. The challenge here will be to identify a plausible source and to find a way to maintain these gases against photodissociation.

Work along these lines is progressing. Recently, Sagan and Chyba [1997] have shown that one way to stabilize NH₃ against photolysis is to shield it from ultraviolet radiation with a layer of organic haze. The haze itself would be the product of CH₄ photolysis. The difficulty here is that such a haze can only be produced in a strongly reducing atmosphere. Alternatively, CH₄ may have played a more direct role by lowering the planetary albedo as well as boosting the greenhouse effect [Kasting, 1997]. However, the required amount ($\sim 1\%$) would almost certainly have to be biological, which raises further issues. Thus a clear solution has yet to emerge [e.g., Kasting and Brown, 1997].

It is also possible that SO₂, a gas which might have been the dominant species in Martian volcanic emissions [Wanke and Dreibus, 1994], and a gas which absorbs strongly in the UV, could prevent CO₂ from condensing in the atmosphere. Yung *et al.* [1997] have shown that 0.1 ppmv of SO₂ in a 2 bar CO₂ atmosphere can raise temperatures in the upper atmosphere enough to prevent CO₂ clouds from forming. Dust particles, which tend to warm the present-day Martian atmosphere [e.g., Pollack *et al.*, 1979], may play a similar role. In both cases, more detailed 3-D modeling is needed to determine to what extent CO₂ condensation can be inhibited by direct heating. In view of the potentially powerful scattering greenhouse effect of CO₂ ice clouds, preventing their occurrence may not be a desirable outcome.

6.3. Warm, Wet Conditions Developed Sporadically

Thus far we have assumed that annual and globally averaged surface temperatures in excess of 273 K are required to stabilize liquid water. However, it is possible to stabilize liquid water at certain times and locations even when global and annual mean temperatures are below freezing. This can occur seasonally when the orbit eccentricity and/or obliquity are near their maximum values [Toon *et al.*, 1980]. For example, at the equator at perihelion when the eccentricity is at its maximum value (~ 0.14) and the solar luminosity is 70% of its present value, the daily averaged insolation is 30% greater than the present solar flux. According to the Pollack *et al.* [1987] calculations shown in Figure 5, only 1 bar of CO₂ is required to produce melting for this case, and Kasting's [1991] condensation constraint should not be a factor for such high insolation.

However, the water-worn features are not limited to the equatorial regions. One way to explain the higher latitude features is to form them at times of high obliquity when the polar insolation is high. The mean obliquity of Mars may have

varied significantly early in its history due to impacts and updoming, which can change the planet's moment of inertia. At high obliquity ($>40^\circ$), polar temperatures at or above freezing are possible [Toon *et al.*, 1980]. Thus changes in the planet's orbital properties are a possible solution, though to what extent these can provide favorable conditions globally is not certain.

Another possibility is that transient warm and wet conditions were caused by large impacts into a water-rich regolith. If much of the impact energy is available to heat the air and vaporize the water, it is quite possible that a transient atmosphere could be formed that would produce warm and wet conditions lasting for days to weeks. What makes this possibility attractive is the fact that most of the valley networks date from the period of heavy bombardment.

Alternatively, a transient SO_2 greenhouse could have been produced during intense volcanic events [Fanale and Postawko, 1995]. This model assumes there is a limited amount of atmospheric water vapor available to oxidize the SO_2 and that once it is gone, SO_2 can build up rapidly if the water resupply rate is small. The validity of these assumptions is uncertain, and there may be sinks for SO_2 other than oxidation by water vapor. Nevertheless, early Mars was likely to have had a much higher rate of volcanic activity than it does today.

6.4. Early Mars Was Cooler Than Presumed

Given the still considerable uncertainty with the above possible solutions, this option needs to be kept open. While the valley networks and the high early erosion rates are often cited as evidence for warm and wet conditions, the actual environmental conditions required to form them are poorly understood (see Baker *et al.* [1992] for an alternative view). This is due to the difficulty with interpreting orbital images. Certain landforms can be produced by a variety of mechanisms. For example, precipitation and runoff, which require a warm, wet climate, are an obvious choice for valley formation, but groundwater sapping [e.g., Pieri, 1980] and mass wasting [Carr, 1996] are processes that do not, and the arguments in favor of them are quite strong. Indeed, Squyres and Kasting [1995] present a picture of early Mars with subfreezing environmental conditions wherein valley formation occurs principally by sapping and hydrothermal convection. Certainly, the higher heat flows expected on early Mars must contribute in some way. Postawko and Fanale [1993] have shown that heat flows greater than 100 mW m^{-2} can raise the depth to the 273 K isotherm to less than 350 m, which would greatly increase the efficiency of valley formation. However, it is not clear that the degraded landforms of the ancient southern highlands can be fully explained by this mechanism. Instead, precipitation may have been involved [Craddock and Maxwell, 1993], but if this is the case, then why aren't the valley networks much more developed than they are? A widely agreed upon mechanism responsible for the early high erosion rates has yet to be identified.

6.5. The Early Sun Was Brighter

By far, the biggest challenge for climate models is coping with the faint young Sun. If the early solar flux was greater than predicted by the standard model, then climate models would be much more consistent with the early warm and wet hypothesis. One way to achieve this is by invoking a more massive zero age main sequence star than we see today. The solar flux is very sensitive to mass ($F \sim M^{4.75}$). Thus, if the early Sun was more

massive than it is today, it would have been brighter than predicted by the standard model.

Boothroyd *et al.* [1991] estimate that a 10% more massive early Sun could explain the 2 orders of magnitude depletion of lithium in the Sun's photosphere. This would allow convection to mix lithium deeper into the Sun's interior, where temperatures would be high enough to destroy it. However, a 10% more massive early Sun poses several problems. First, the solar flux arriving at Earth would be more than 50% brighter than it is today, which is high enough to evaporate the oceans through the runaway moist greenhouse effect [Kasting, 1988]. Second, it implies early mass loss rates for solar-type stars that are 10^4 times the present solar wind. Whitmire *et al.* [1995] reexamined this issue and suggested that a 5% more massive early Sun could satisfy the constraints and lead to loss rates about an order of magnitude smaller. Though this solution is not widely accepted, it cannot be ruled out, since mass loss rates 10^3 times the present value are still very difficult to detect. Thus a systematic search for young solar-like stars with these kinds of mass loss rates needs to be undertaken.

7. Summary

The discovery of apparent fluvial features in Mariner 9 images of the surface of Mars in the early 1970s has led to speculation that climatic conditions on early Mars were warmer and wetter than they are today. Since then, a number of climate models have been developed to explain these conditions in terms of a greenhouse effect. The principal challenge for these models has been to produce global mean surface temperatures of 273 K at a time when the solar luminosity was 75% of its present value. Ammonia was originally suggested as the greenhouse gas because of its absorption features in the window region and because its photolysis products are biogenic precursors. However, it was later rejected because of its short photochemical lifetime. Subsequently, more oxidizing atmospheres of CO_2 and H_2O were considered. By the end of the 1980s, it was believed that a 5 bar CO_2 atmosphere, maintained by volcanism and impacts, could sustain warm and wet conditions long enough to form the valley networks and erode the ancient southern highlands [Pollack *et al.*, 1987].

However, in the 1990s the warm and wet hypothesis was challenged when it was recognized that CO_2 would condense in the atmosphere and that this would limit both the size of the atmosphere and its greenhouse potential [Kasting, 1991]. This condensation constraint limits the early Mars atmosphere to no more than 2.5 bars of CO_2 , and global mean surface temperatures to no higher than 220 K. Additional, but less serious, challenges to the warm and wet hypothesis stem from the disposal of such a massive early atmosphere. As much as 80 m of globally distributed calcite must reside near the surface, yet carbonates have been difficult to detect thus far. And no evolutionary scenario has been found yet that begins with a massive CO_2 atmosphere and ends with the atmosphere/cap system we see today.

Several mechanisms have been suggested to deal with this condensation constraint. One eliminates the CO_2 clouds by invoking heating of the atmosphere due to the absorption of ultraviolet radiation by small amounts of SO_2 [Yung *et al.*, 1997]. The other exploits the presence of CO_2 clouds by showing that they can reflect infrared radiation back to the surface [Forget and Pierrehumbert, 1997]. While each mechanism is

promising, more detailed 3-D modeling is needed to better assess their potential for warming early Mars.

Thus, at the present time, we do not have a self-consistent robust theory for how early Mars could have a sustained a warm and wet climate for an extended period of time. Given the history of our views on this issue, it would be prudent to hold open the option that the valley networks and degraded terrains somehow formed in a cool environment. If true, it would imply that conditions for the origin of life on early Mars were harsher than previously believed. However, it must be emphasized that the evidence for liquid water on the surface of Mars early in its history is compelling; only the interpretation of the prevailing climate is uncertain. Mars remains therefore an important target for exobiological investigations.

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